



Stochastic efficiencies

G. Verley, M. Esposito, T. Willaert and C. Van den Broeck
The unlikely Carnot efficiency
Nature Communications DOI: 10.1038/ncomms5721
(2014)

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Universal theory of efficiency fluctuations
Phys. Rev. E 90, 052145 (2014).

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Stochastic efficiency for effusion as a thermal engine
EPL 109, 20004 (2015).

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S. Rana, P. Pal, A. Saha, and A. Jayannavar,
Physical Review E 90, 042146 (2014).

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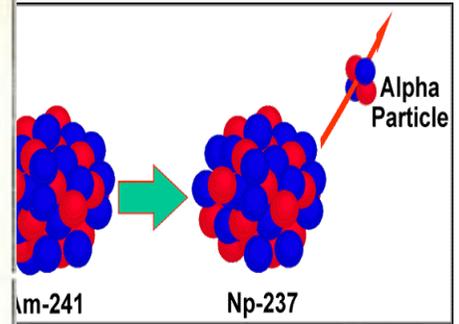
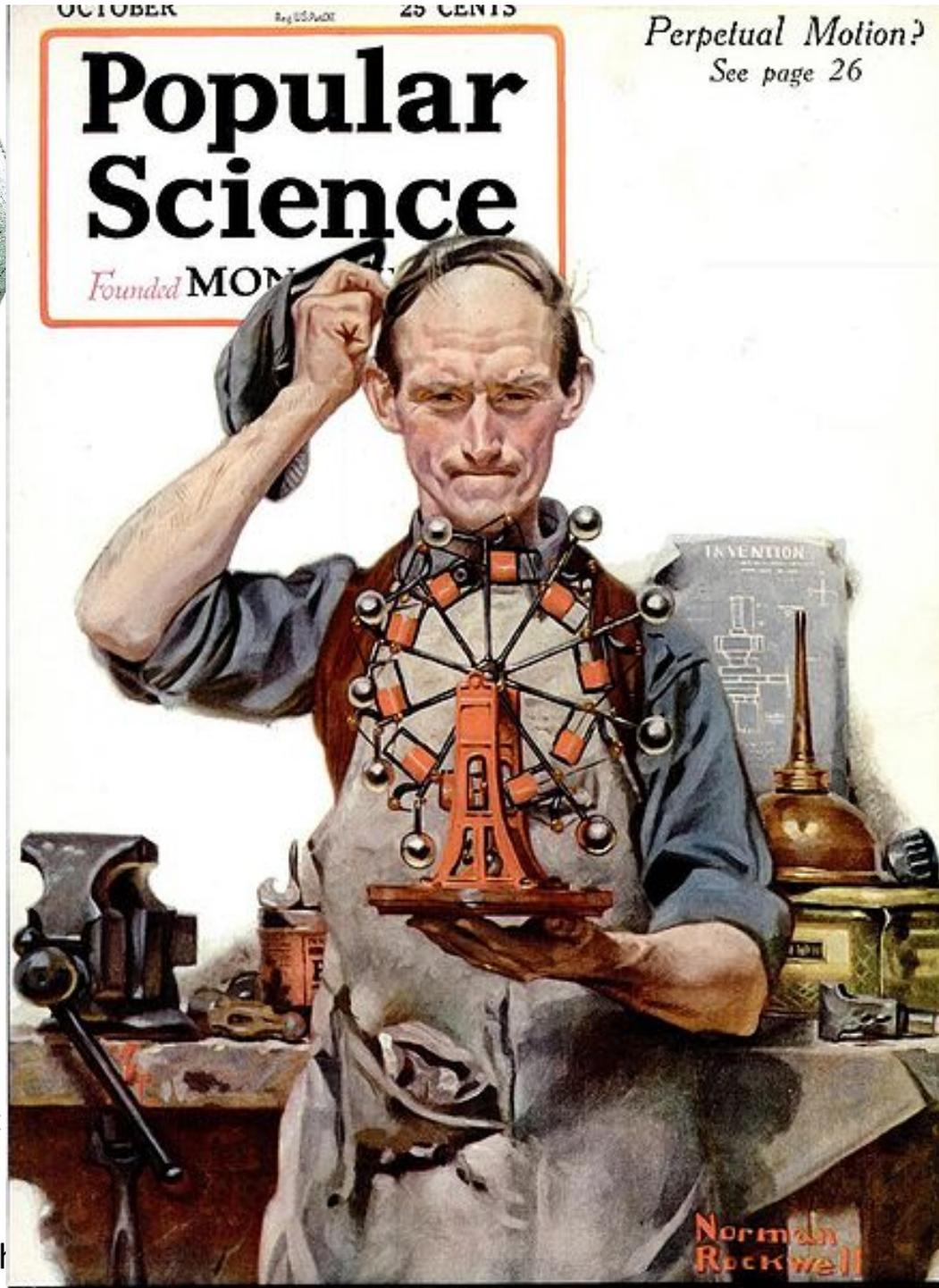
S. Rana, P. Pal, A. Saha, and A. Jayannavar,
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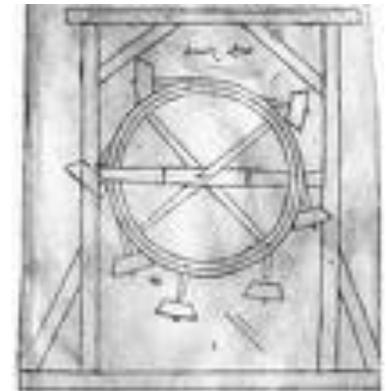
elixir
of life



Pierre de Maricourt
(about 1270)

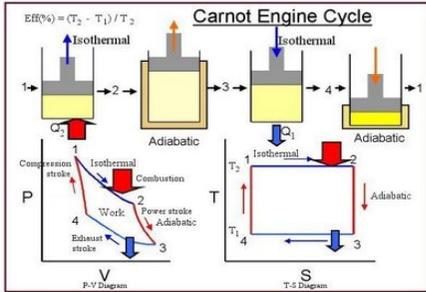


transmutation
elements



Villard de Honnecourt
(about 1230)

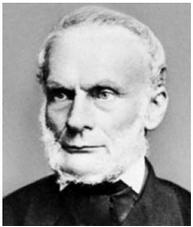
Efficiency: heat to work



Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance.

$$\eta = \frac{\text{output work } W}{\text{input heat } Q_h} \leq \eta_c = 1 - \frac{T_c}{T_h}$$

Carnot Efficiency



$$\oint_{qs} \frac{dQ}{T} = 0$$

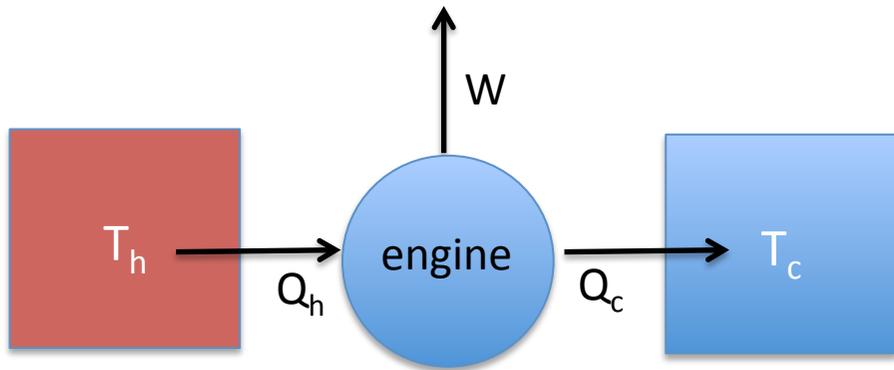
$$\Delta S = \int_{qs} \frac{dQ}{T}$$



Ueber die bewegende Kraft der Wärme und die Gesetze, welche sich daraus für die Wärme selbst ableiten lassen

$$\Delta S_{tot} \geq 0$$

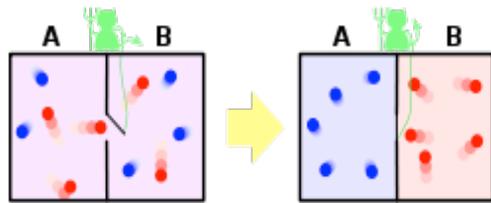
2nd law



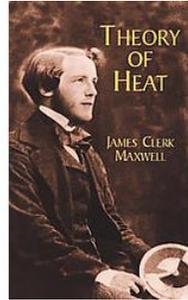
1st law $W = Q_h - Q_c - \Delta S$ ~~X~~

2nd law $\Delta S_{tot} = \frac{-Q_h}{T_h} + \frac{Q_c}{T_c} + \Delta S \geq 0$ ~~X~~

$$\eta = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \leq \eta_c = 1 - \frac{T_c}{T_h}$$

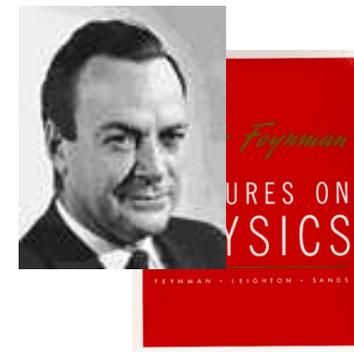
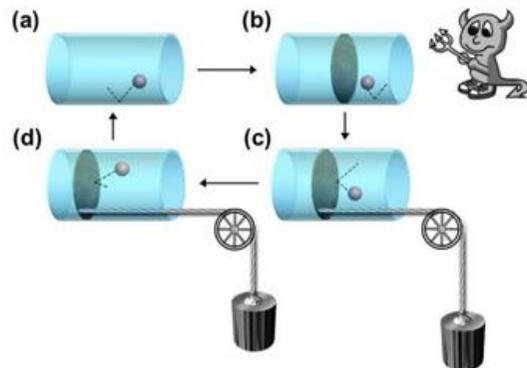
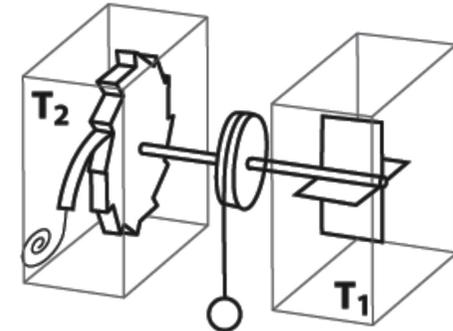


Maxwell demon



M. v. Smoluchowski (Leuberg). *Experimentell nachweisbare, der üblichen Thermodynamik widersprechende Molekularphänomene*

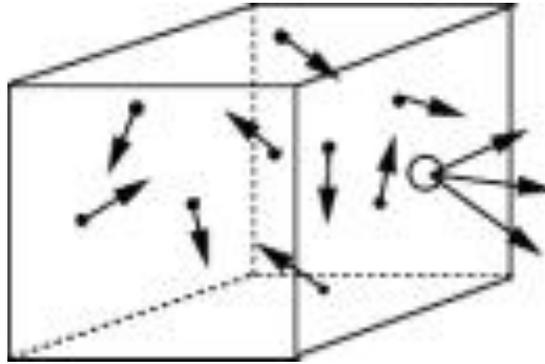
... Theoretisch noch einfacher und übersichtlicher ist das Beispiel des Torsionsfadens. Binden wir anstatt des Spiegels unten ein Zahnrad mit einer Sperrklappe (mit Zwangsleitung) an, welche nur einseitige Drehung zulässt, infolge der fortwährenden Schwankungen wird das Zahnrad eine Drehung, der Faden eine Torsion erfahren, welche öfters zu nutzbarer Arbeit im Aufhängepunkt verwendet werden könnte. Es wäre diese Vorrichtung analog einer Spielbank, welche die Gesetze des Zufalls systematisch korrigiert. Die Schwierigkeit der technischen Ausführung bildet da keinen Einwand, wenn die Sache prinzipiell möglich ist.



Szilard engine $1 \text{ bit} = kT \ln 2$



Thomas Graham



Flux $1/\sqrt{M}$ enrichment

Energy $2k_B T$ cooling

Cosine law deposition



Martin Knudsen

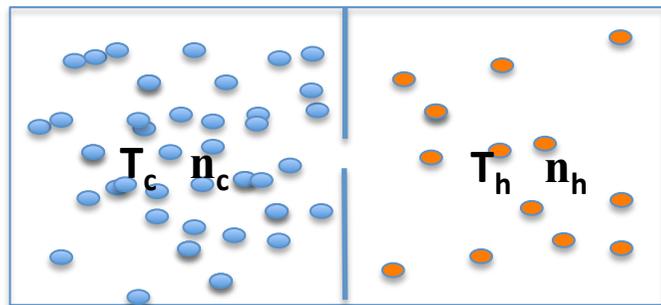
EFFUSION
as a thermal engine

$$\Delta E = Q + W$$

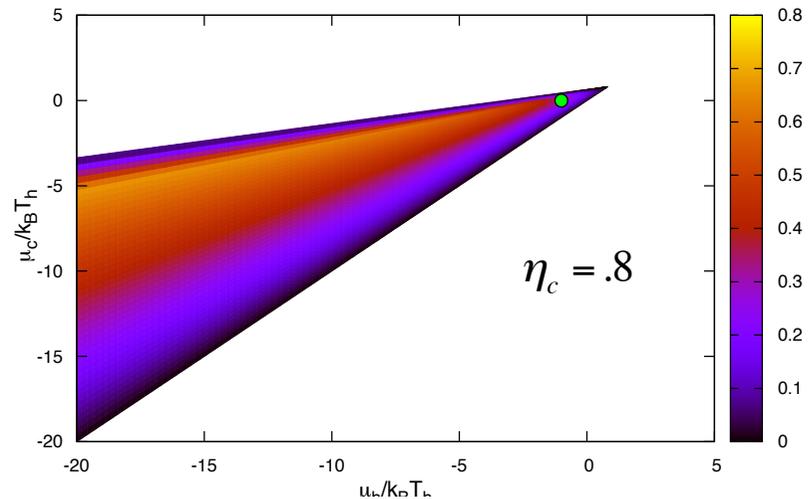
$$W = \mu \Delta N$$

efficiency η

$$\eta = \frac{W}{Q_h} = \frac{(\mu_c - \mu_h) \langle \Delta N \rangle}{\langle \Delta e \rangle - \mu_h \langle \Delta N \rangle} \leq 1 - \frac{T_c}{T_h} = \eta_C$$

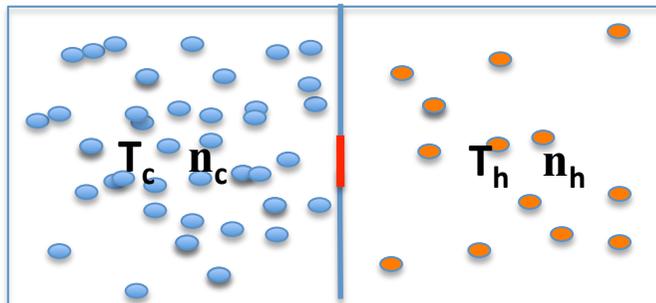


$\Delta N, \Delta E$



EFFUSION
as a thermal engine
reaching Carnot efficiency?

reversible operation: *filter specific speed* v |
particle density with speed v same left and right



←
 $\Delta N, \Delta E$

$$\frac{n_c}{T_c^{3/2}} \exp\left(-\frac{mv^2}{2kT_c}\right) = \frac{n_h}{T_h^{3/2}} \exp\left(-\frac{mv^2}{2kT_h}\right)$$

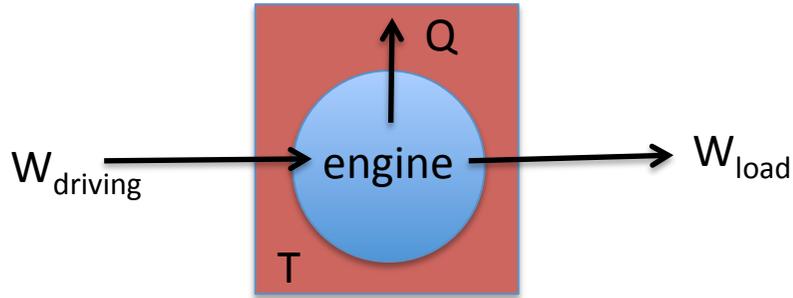
$$\mu = kT \ln n \sqrt{h^2 / 2\pi mkT}^3$$

$$e^{-\beta_c(\frac{mv^2}{2} - \mu_c)} = e^{-\beta_h(\frac{mv^2}{2} - \mu_h)} \quad \mu_c - \mu_h = \eta_c \left(\frac{mv^2}{2} - \mu_h\right)$$

$$\Delta E = \Delta N \frac{mv^2}{2}$$

$$\eta = \frac{W}{Q_h} = \frac{(\mu_c - \mu_h) \Delta N}{\langle \Delta E \rangle - \mu_h \Delta N} = \frac{\mu_c - \mu_h}{mv^2 / 2 - \mu_h} = \eta_c = 1 - \frac{T_c}{T_h}$$

Efficiency: Work to Work Engine

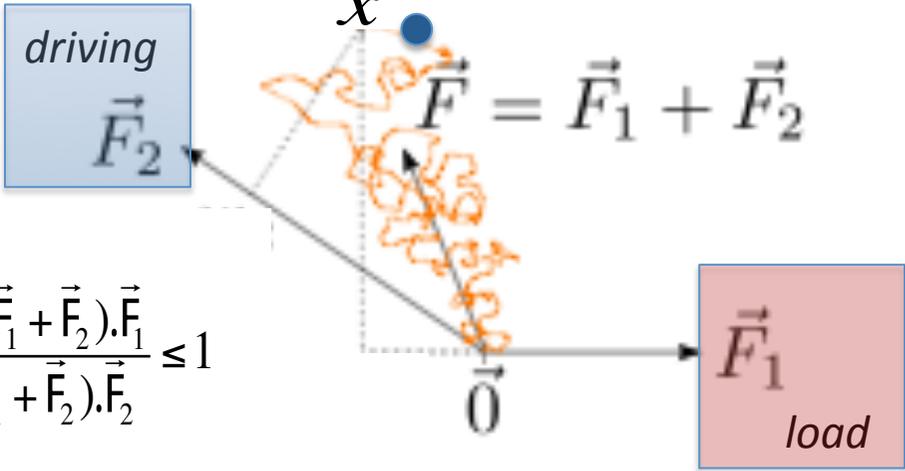


1st law $W_{load} = W_{driving} - Q - \cancel{\Delta E}$

2nd law $\Delta S_{tot} = \frac{Q}{T} + \cancel{\Delta S} \geq 0$

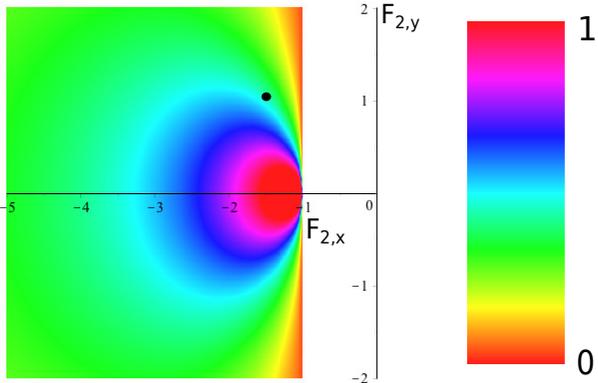
$\eta = \frac{W_{load}}{W_{driving}} = 1 - \frac{Q}{W_{driving}} \leq \eta_{rev} = 1$

Brownian particle
 F_1 (load) F_2 (driving)



$$\text{efficiency } \eta = \frac{W_{load}}{W_{driving}} = \frac{\langle w_{load} \rangle}{\langle w_{driving} \rangle} = \frac{-\langle \vec{x} \rangle \cdot \vec{F}_1}{\langle \vec{x} \rangle \cdot \vec{F}_2} = \frac{-(\vec{F}_1 + \vec{F}_2) \cdot \vec{F}_1}{(\vec{F}_1 + \vec{F}_2) \cdot \vec{F}_2} \leq 1$$

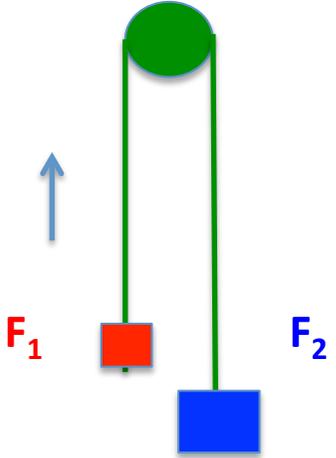
$$\langle \vec{x} \rangle = \frac{t(\vec{F}_1 + \vec{F}_2)}{\gamma}$$



reversible operation

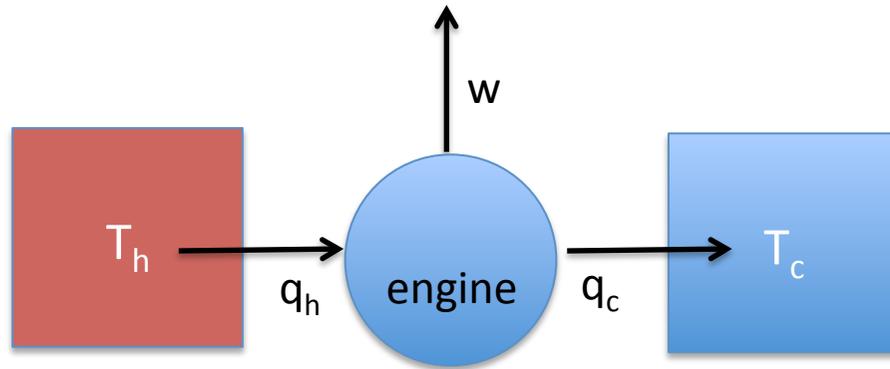
$\vec{F}_1 \rightarrow -\vec{F}_2$

$\eta = 1 = \eta_{rev}$



Stochastic efficiency of small engines?

$$\bar{\eta} = \frac{W}{Q_h} = \frac{\langle w \rangle}{\langle q_h \rangle} \quad \text{versus} \quad \eta = \frac{w}{q_h}$$



1st law $w = q_h - q_c$ ~~$-T_c \Delta s$~~

2nd law $\Delta s_{tot} = \frac{-q_h}{T_h} + \frac{q_c}{T_c} + \Delta s$ ~~Δs~~

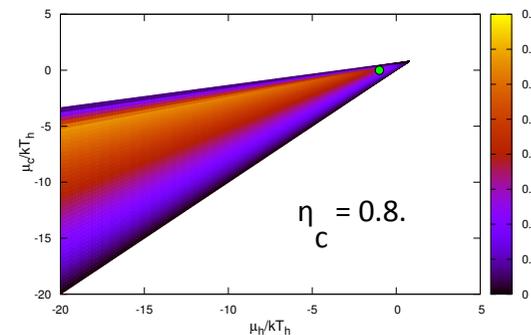
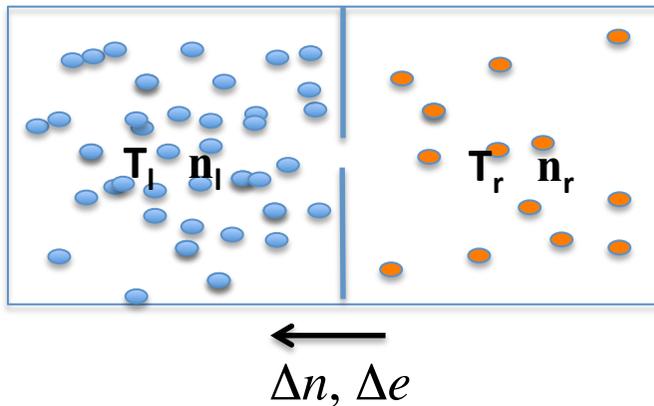
$\langle \Delta s_{tot} \rangle \geq 0$

$$\eta = \frac{w}{q_h} \stackrel{1st \text{ law}}{=} 1 - \frac{q_c}{q_h} \stackrel{2nd \text{ law}}{=} \eta_C - \frac{T_c \Delta s_{tot}}{q_h}$$

$$\Delta s_{tot} = 0 \rightarrow \eta = \eta_C$$

$$\left. \begin{array}{l} P_t(\Delta s_{tot}) \\ P_t(w, q_h) \end{array} \right\} \rightarrow P_t(\eta)$$

**Heat to work:
effusion engine**

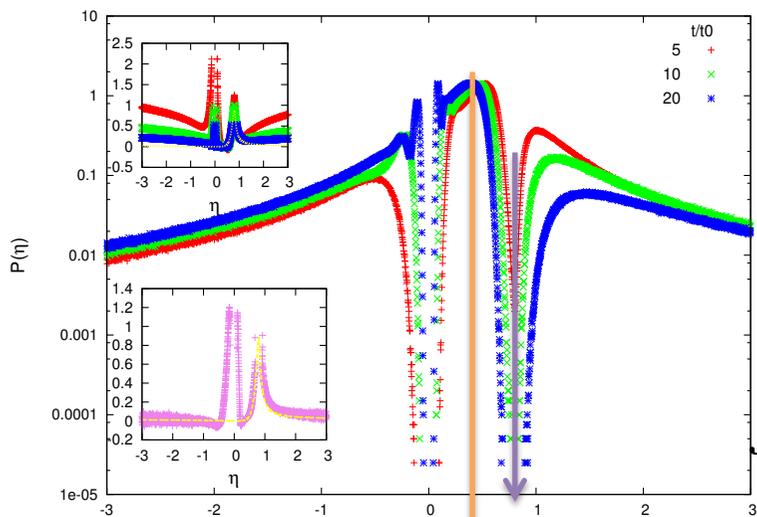


$$\eta = \frac{w}{q_h} = \frac{(\mu_c - \mu_h) \Delta n}{\Delta e - \mu_h \Delta n}$$

kinetic theory $\rightarrow P_t(\Delta n, \Delta e) \rightarrow P_t(\eta)$

$P_t(\eta)$

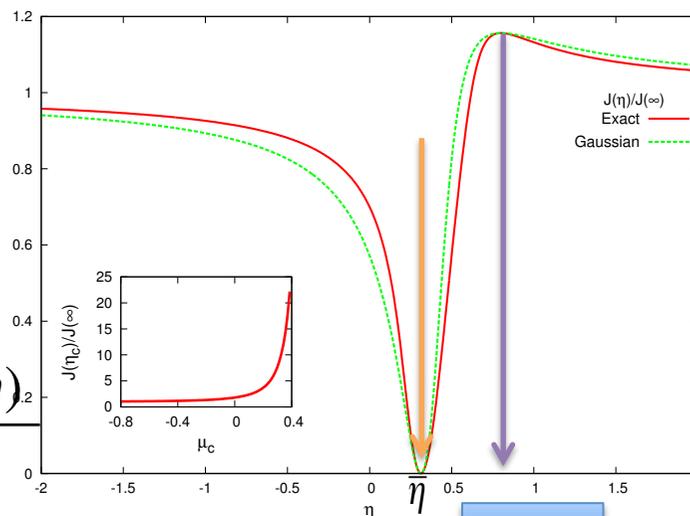
$J(\eta)$



$$P_t(\eta) \propto e^{-tJ(\eta)}$$

large
deviation
function

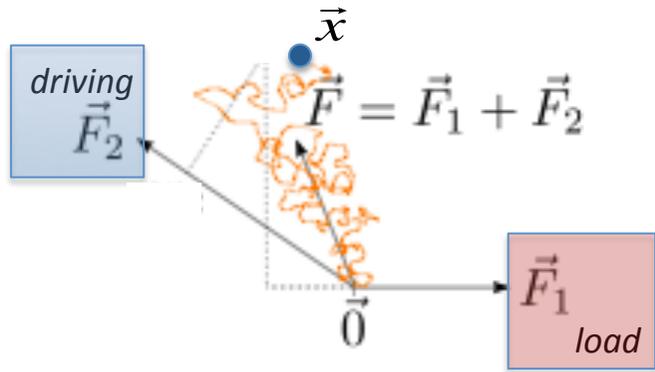
$$J(\eta) = -\lim_{t \rightarrow \infty} \frac{\ln P_t(\eta)}{t}$$



(b) $\bar{\eta} \approx 0.4$

(a) $\eta_c = 0.8$

Work to work:
Brownian particle
F₁ (load) F₂ (driving)



\vec{x} : Brownian motion in force field $\vec{F} = \vec{F}_1 + \vec{F}_2$

\vec{x} bi-Gaussian $\langle \vec{x} \rangle = \frac{\vec{F}}{\gamma} t$ $\langle \delta \vec{x} \cdot \delta \vec{x} \rangle = 2Dt \vec{1}$

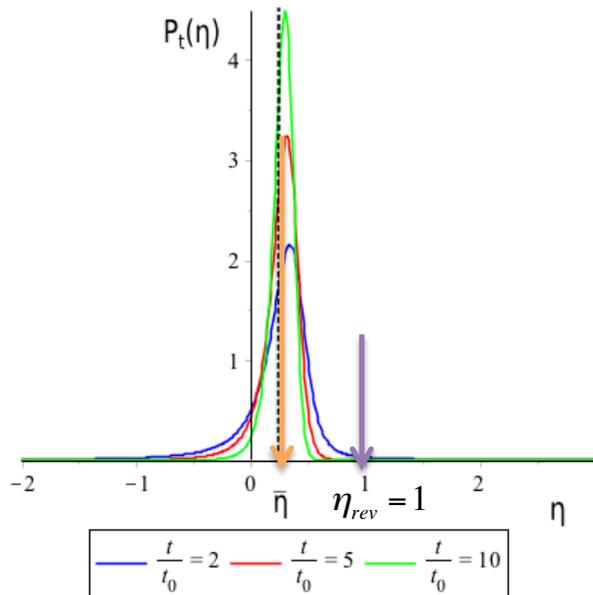
$\eta = \frac{-\vec{F}_1 \cdot \vec{x}}{\vec{F}_2 \cdot \vec{x}}$ ratio of correlated Gaussians

$$P_t(\eta) = \frac{|\vec{F}_1 \times \vec{F}_2| e^{-\frac{t}{t_0}}}{\pi(\vec{F}_1 + \eta \vec{F}_2)^2} \left(1 + \sqrt{\pi g(\eta)} \text{Erf} \left[\sqrt{g(\eta)} \right] e^{g(\eta)} \right)$$

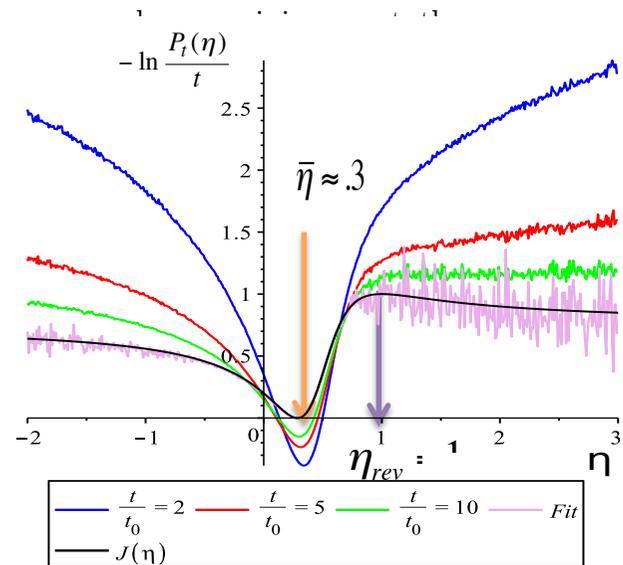
$$g(\eta) = \frac{t}{t_0} \frac{(1-\eta)^2 (\vec{F}_1 \times \vec{F}_2)^2}{\vec{F}_2^2 (\vec{F}_1 + \eta \vec{F}_2)^2}$$

$$J(\eta) = - \lim_{t \rightarrow \infty} \frac{1}{t} \ln P_t(\eta)$$

$$= \frac{\mu^2 \left[(\vec{F}_1 + \eta \vec{F}_2) \cdot (\vec{F}_1 + \vec{F}_2) \right]^2}{4D (\vec{F}_1 + \eta \vec{F}_2)^2}$$

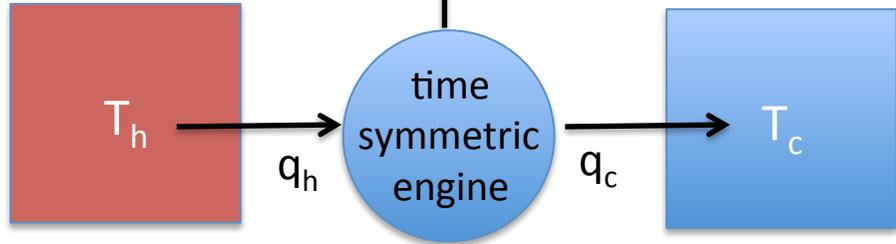


$$P_t(\eta) \propto e^{-tJ(\eta)}$$



time symmetric engine

Stochastic thermodynamics



1st law $w = q_h - q_c$ ~~$- \Delta s$~~

2nd law $\Delta s_{tot} = \frac{-q_h}{T_h} + \frac{q_c}{T_c} + \Delta s$ ~~$- \Delta s$~~

$$\frac{P(q_h, w)}{P(-q_h, -w)} \propto e^{\Delta s_{tot}}$$

$$P(q_h, w) \propto e^{-tI(\dot{q}_h, \dot{w})}$$

$$I(\dot{q}_h, \dot{w}) - I(-\dot{q}_h, -\dot{w}) = -\Delta s_{tot} / t$$

$$\eta = w / q_h = \dot{w} / \dot{q}_h$$

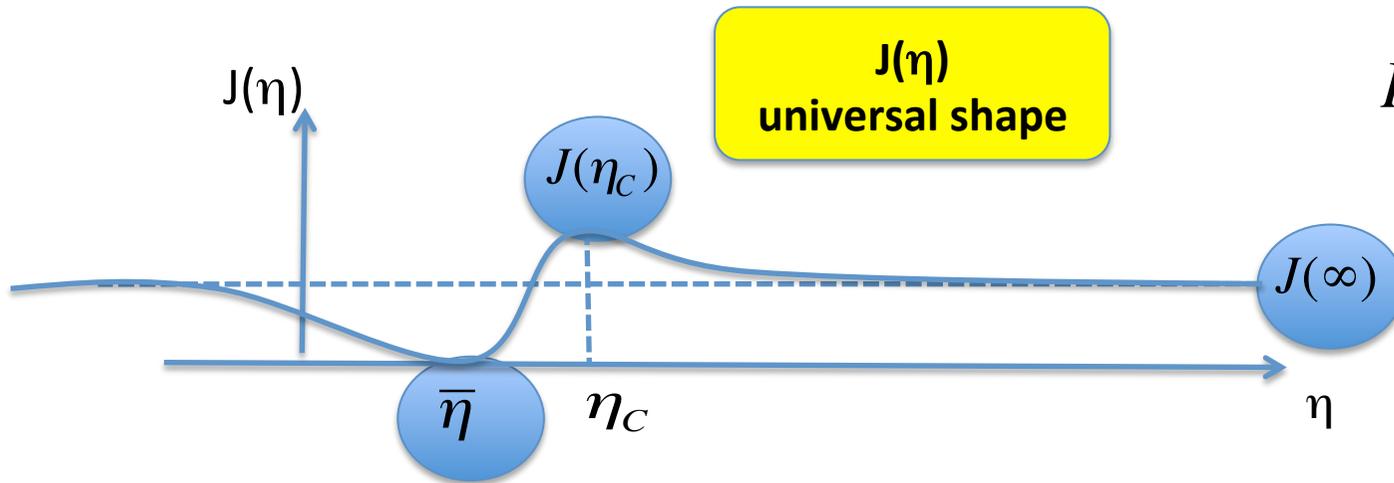
$$P_t(\eta) \propto e^{-tJ(\eta)}$$

$$J(\eta) = \min_{\dot{q}_h, \dot{w}}_{\eta = \dot{w} / \dot{q}_h} I(\dot{q}_h, \dot{w})$$

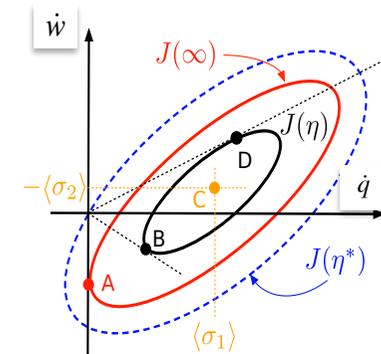
$$J(\eta) = \min_{\dot{q}_h, \dot{w}}_{\eta = \dot{w} / \dot{q}_h} I(\dot{q}_h, \dot{w}) = \min_{\dot{q}_h} I(\dot{q}_h, \eta \dot{q}_h) \leq I(0, 0)$$

$$\Delta s_{tot} = 0 \rightarrow \begin{matrix} \eta = w / q_h = \eta_c \\ I(\dot{q}_h, \dot{w}) \text{ symmetric} \end{matrix} \rightarrow J(\eta_c) = \min I(\dot{q}_h, \eta_c \dot{q}_h) = I(0, 0) \geq J(\eta)$$

The Carnot efficiency is the least likely to be observed in the long time limit!



$$P_t(\eta) \propto e^{-tJ(\eta)}$$



**close to equilibrium
universal scaling form**

featuring Onsager coefficients L_{11} L_{22} $L_{12}=L_{21}$

$$\frac{J(\eta)}{J(\eta_c)} = \frac{(\bar{\eta} - \eta)^2}{(\bar{\eta} - 2\eta + \eta_c)(\bar{\eta} - \eta_c) + \frac{J(\eta_c)}{J(\infty)}(\eta - \eta_c)^2}$$

**J(η) unusual
large deviation function**

$$P(\eta) \propto \frac{\int P(w, 0) |w| dw}{\eta^2}$$

$$\frac{1}{\det C} \begin{bmatrix} C_{qq} & -C_{wq} \\ -C_{wq} & C_{ww} \end{bmatrix} \begin{pmatrix} \dot{W} \\ \dot{Q} \end{pmatrix} = \begin{pmatrix} 1/2T_c \\ \eta_c/(2T_c) \end{pmatrix}$$

$$C_{qq} = \frac{8J(\eta_c)^2 T_c^2}{(\bar{\eta} - \eta_c)^2 J(\infty)},$$

$$C_{wq} = -8J(\eta_c) T_c^2 \frac{J(\infty)\bar{\eta} - J(\infty)\eta_c + \eta_c J(\eta_c)}{J(\infty)(\bar{\eta}^2 - 2\bar{\eta}\eta_c + \eta_c^2)},$$

$$C_{ww} = 8J(\eta_c) T_c^2 \frac{J(\infty)\bar{\eta}^2 + \eta_c^2 J(\eta_c) - J(\infty)\eta_c^2}{J(\infty)(\bar{\eta}^2 - 2\bar{\eta}\eta_c + \eta_c^2)}.$$

$$P_t(\eta) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_t(w, q) \delta\left(\eta - \frac{w}{q}\right) dw dq$$

$$= \int_{-\infty}^{\infty} P_t\left(w, \frac{w}{\eta}\right) \left| \frac{w}{\eta^2} \right| dw,$$

time asymmetric engine

1st law $w = q_h - q_c - \cancel{L\Delta s}$

2nd law $\Delta s_{tot} = \frac{-q_h}{T_h} + \frac{q_c}{T_c} + \cancel{L\Delta s}$

$P_t(\eta) \propto e^{-tJ(\eta)}$ $\tilde{P}_t(\eta) \propto e^{-t\tilde{J}(\eta)}$

$\frac{P(q_h, w)}{\tilde{P}(-q_h, -w)} \propto e^{\Delta s_{tot}}$

J and \tilde{J} cross in η_c same asymptotes same maximum

Single particle Carnot engine

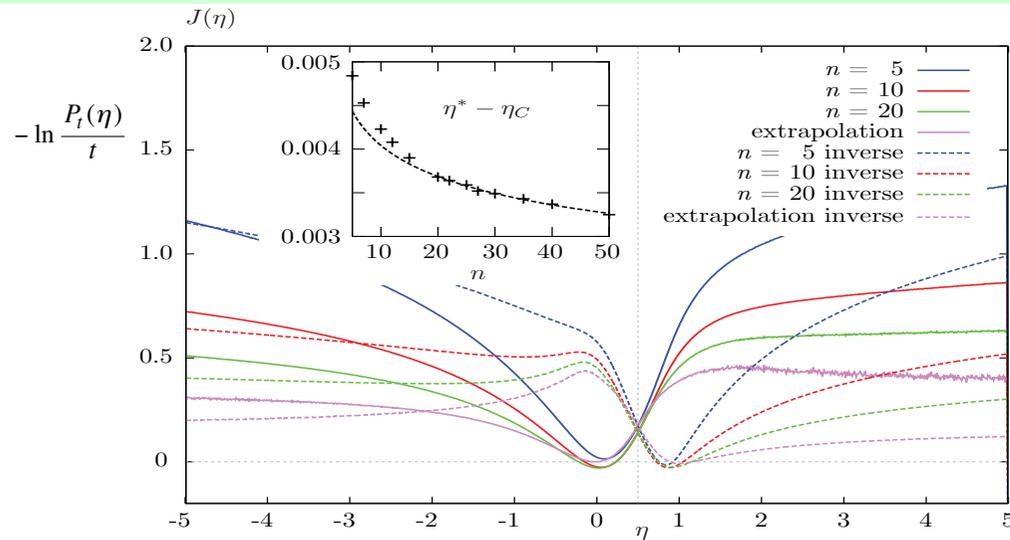
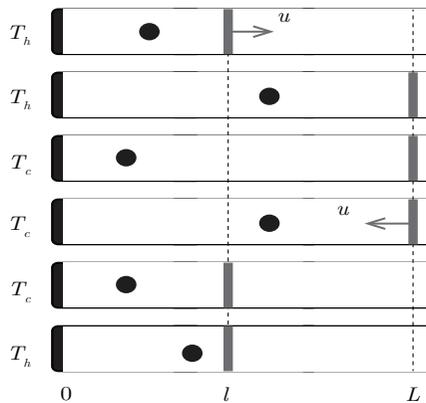
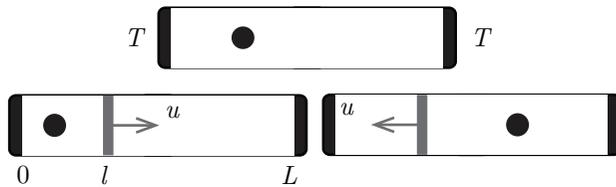


Figure 6: $-(1/n) \ln P_n(\eta)$ for 5 (blue), 10 (red) and 20 (green) cycles of the heat engine and its time-inverse, with $T_h = 2T_c$ (i.e. $\eta_C = 1/2$), $u = 0.3$ and $x = 0.5$. The purple curve is the extrapolation to the LDF. The macroscopic efficiency is given by $\bar{\eta} = -0.02$ Inset: convergence of the intersections efficiency η^* of forward and time-reverse curves to η_C as the number n of cycles increases. The dashed line is a power law fit of the form α/n^β , with $\alpha = 5.49 \cdot 10^{-3}$ and $\beta = 0.13$

Information to work Szilard engine

$$\eta = \frac{w}{k_B T \Delta i}$$



$$\Delta i = -\ln \frac{l}{L}$$

$$\Delta i = -\ln \frac{L-l}{L}$$

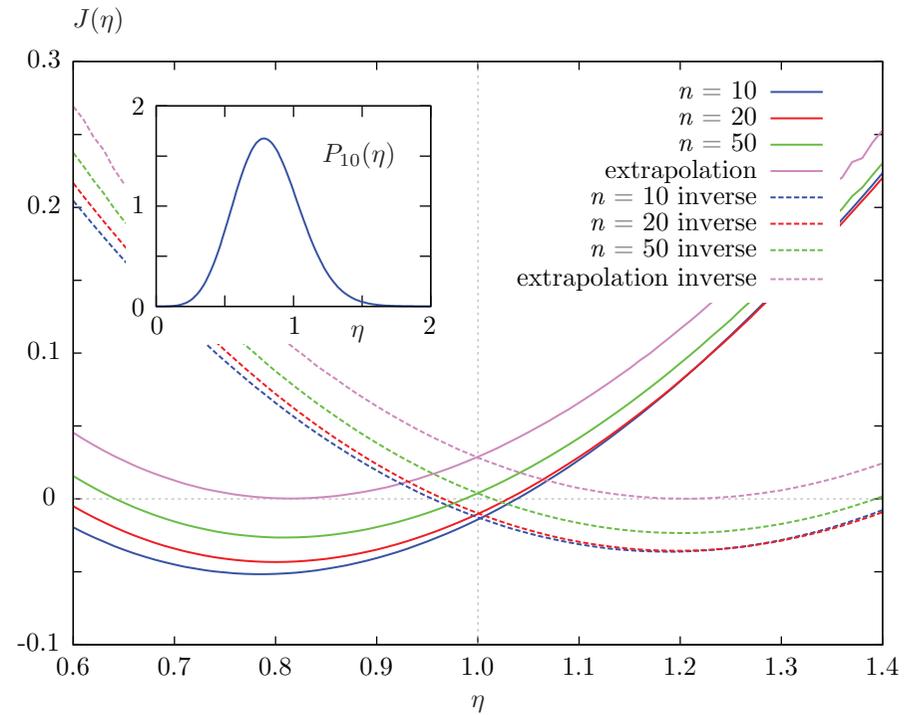
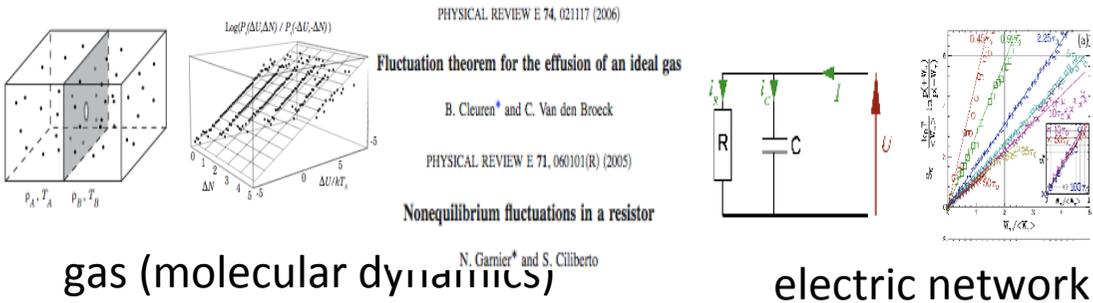
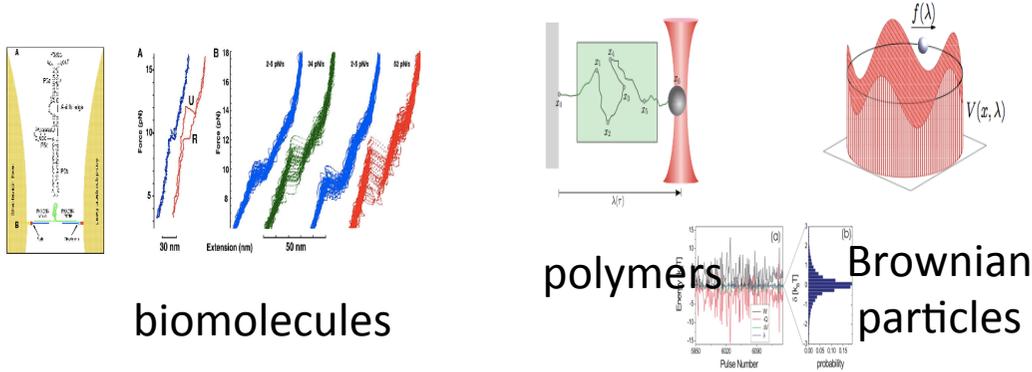


Figure 5: $-(1/n) \ln P_n(\eta)$ for 10 (blue), 20 (red) and 50 (green) cycles of the Szilard engine and its time-inverse, with $u = 0.1$ and $x = 0.7$. The purple curve is the extrapolation to the LDF. The macroscopic efficiency is $\bar{\eta} = 0.80$. The inset shows $P_{10}(\eta)$.

Stochastic work w and heat q hence stochastic efficiency $\eta=w/q$ can be measured!

[Liphardt et al, Science 296 1832, 2002.

V. Blickle, T. Speck, L. Helden, U.S., C. Bechinger, PRL 96, 070603, 2006]



Brownian Carnot engine

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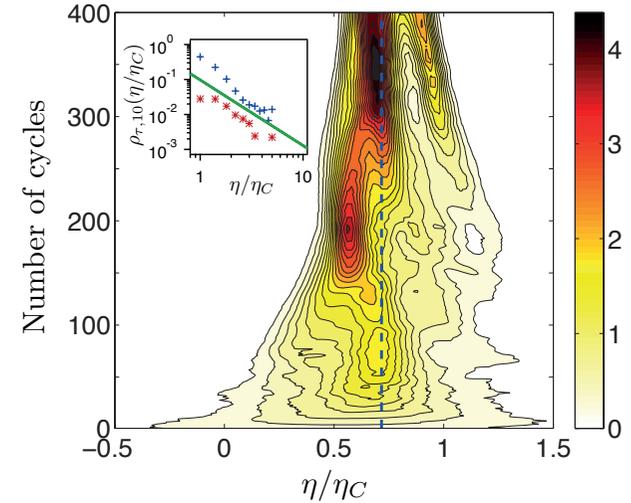
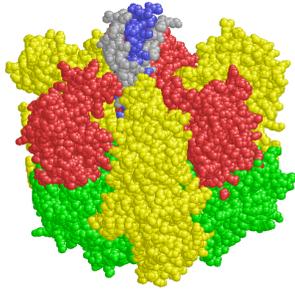


FIG. 3: **Efficiency fluctuations at maximum power.** Contour plot of the probability density function of the efficiency $\rho_{\tau=40 \text{ ms}, i}(\eta)$ computed summing over $i = 1$ to 400 cycles (left axis). The long-term efficiency (averaged over $\tau_{\text{exp}} = 50 \text{ s}$) is shown with a vertical blue dashed line. Super Carnot efficiencies appear even far from quasistatic driving. *Inset:* Tails of the distribution for $\rho_{\tau=40 \text{ ms}, 10}(\eta)$ (blue squares, positive tail; red circles, negative tail). The green line is a fit to a power-law to all the data shown, whose exponent is $\gamma = (-1.9 \pm 0.3)$.

bimodality
 $P(\eta) \sim 1/\eta$



$$\frac{P(\Delta S_{tot})}{\tilde{P}(-\Delta S_{tot})} \propto e^{\Delta S_{tot}/k_B}$$

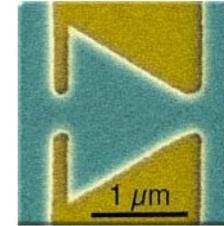
**stochastic efficiency
first + second law**

$$P(\eta) \propto e^{-tJ(\eta)}$$

**time symmetric engine:
reversible efficiency is least likely
universal scaling form near equilibrium**

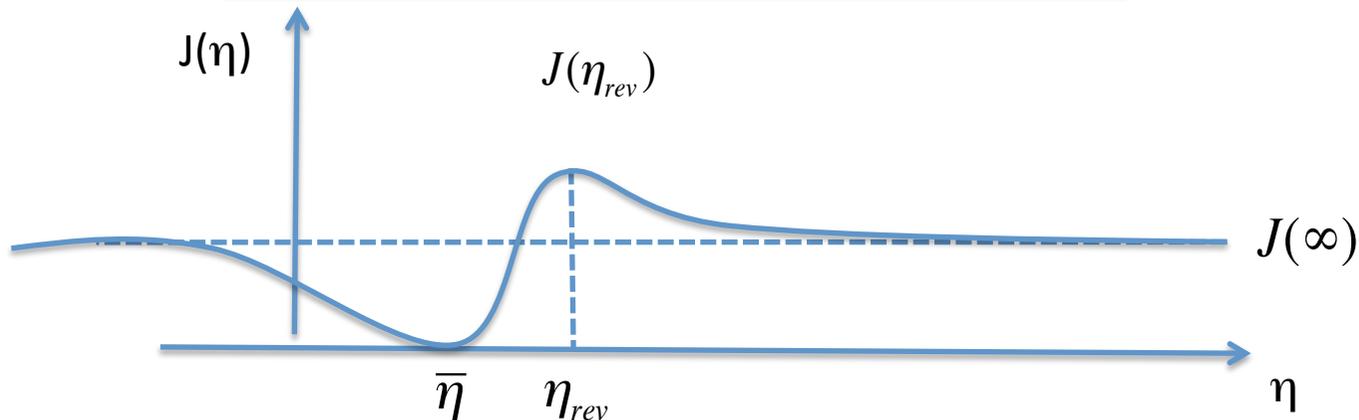
**time asymmetric engine:
crossing at reversible efficiency
maxima equally unlikely, same asymptotes**

**absolute temperature measurement
in nonequilibrium experiment**



Electron microscopic image of a quantum dot ratchet

$$\langle e^{-\Delta S_{tot}/k_B} \rangle = 1$$





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